ORIGINAL PATENT APPLICATION BASED ON:

DEVICE AND METHOD FOR VAPORIZING TEMPERATURE SENSITIVE MATERIALS

DEVICE AND METHOD FOR VAPORIZING TEMPERATURE SENSITIVE MATERIALS

CROSS REFERENCE TO RELATED APPLICATIONS

Reference is made to commonly assigned U.S. Patent Application Serial No. 10/352,558 filed January 28, 2003 by Jeremy M. Grace et al., entitled "Method of Designing a Thermal Physical Vapor Deposition System", the disclosure of which is herein incorporated by reference.

FIELD OF THE INVENTION

The present invention relates to the field of physical vapor deposition where a source material is heated to a temperature so as to cause vaporization and produce a vapor plume to form a thin film on a surface of a substrate.

BACKGROUND OF THE INVENTION

An OLED device includes a substrate, an anode, a hole-transporting layer made of an organic compound, an organic luminescent layer with suitable dopants, an organic electron-transporting layer, and a cathode. OLED devices are attractive because of their low driving voltage, high luminance, wide-angle viewing and capability for full-color flat emission displays. Tang et al. described this multilayer OLED device in their U.S. Patents 4,769,292 and 4,885,211.

Physical vapor deposition in a vacuum environment is the principal way of depositing thin organic material films as used in small molecule OLED devices. Such methods are well known, for example, Barr in U.S. 2,447,789 and Tanabe et al. in EP 0 982 411. The organic materials used in the manufacture of OLED devices are often subject to degradation when maintained at or near the desired rate-dependent vaporization temperature for extended periods of time. Exposure of sensitive organic materials to higher temperatures can cause changes in the structure of the molecules and associated changes in material properties.

To overcome the thermal sensitivity of these materials, only small quantities of organic materials have been loaded in sources, and they are heated as little as possible. In this manner, the material is consumed before it has reached

the temperature exposure threshold to cause significant degradation. The limitations with this practice are that the available vaporization rate is very low due to the limitation on heater temperature, and the operation time of the source is very short due to the small quantity of material present in the source. The low deposition rate and frequent source recharging place substantial limitations on the throughput of OLED manufacturing facilities.

A secondary consequence of heating the entire organic material charge to roughly the same temperature is that it is impractical to mix additional organic materials, such as dopants, with a host material unless the vaporization behavior and vapor pressure of the dopant is very close to that of the host material. This is generally not the case and, as a result, prior art devices frequently require the use of separate sources to co-deposit host and dopant materials.

The organic materials used in OLED devices have a highly non-linear vaporization rate dependence on source temperature. A small change in source temperature leads to a very large change in vaporization rate. Despite this, prior art devices employ source temperature as the only way to control vaporization rate. To achieve good temperature control, prior art deposition sources typically utilize heating structures whose solid volume is much larger than the organic charge volume, composed of high thermal-conductivity materials that are well insulated. The high thermal conductivity insures good temperature uniformity through the structure, and the large thermal mass helps to maintain the temperature within a critically small range by reducing temperature fluctuations. These measures have the desired effect on steady-state vaporization rate stability but have a detrimental effect at start-up. It is common that these devices must operate for many hours at start-up before steady-state thermal equilibrium and hence a steady vaporization rate is achieved.

A further limitation of prior art sources is that the geometry of the vapor manifold changes as the organic material charge is consumed. This change requires that the heater temperature change to maintain a constant vaporization rate, and it is observed that the plume shape of the vapor exiting the orifices

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changes as a function of the organic material thickness and distribution in the source.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a device and method for vaporizing organic materials while limiting their exposure to temperatures that can cause material degradation. It is a further object of this invention to permit a single source to deposit two or more organic material components. It is a further object of this invention to achieve a steady vaporization rate quickly. It is a further object to maintain a steady vaporization rate with a large charge of organic material and with a steady heater temperature.

This object is achieved by a method for vaporizing organic materials onto a substrate surface to form a film, comprising:

a) providing a quantity of organic material into a vaporization apparatus;

b) actively maintaining the organic material in a first heating region in the vaporization apparatus to be below the vaporization temperature;

c) heating a second heating region of the vaporization apparatus above the vaporization temperature of the organic material; and

d) metering, at a controlled rate, organic material from the first region into the second heating region so that a thin cross section of the organic material is heated at a desired rate-dependent vaporization temperature, whereby organic material sublimes and forms a film on the substrate surface.

ADVANTAGES

It is an advantage of the present invention that the device overcomes the heating and volume limitations of prior art devices in that only a small portion of organic material is heated to the desired rate-dependent vaporization temperature at a controlled rate. It is therefore a feature of the present invention to maintain a steady vaporization rate with a large charge of organic material and with a steady heater temperature. The device thus permits extended operation of the source with substantially reduced risk of degrading even very temperature sensitive organic materials. This feature additionally permits materials

having different vaporization rates and degradation temperature thresholds to be co-sublimated in the same source.

It is a further advantage of the present invention that it permits finer rate control and additionally offers an independent measure of the vaporization rate.

It is a further advantage of the present invention that it can be cooled and reheated in a matter of seconds to stop and reinitiate vaporization and achieve a steady vaporization rate quickly. This feature minimizes contamination of the deposition chamber walls and conserves the organic materials when a substrate is not being coated.

It is a further advantage that the present device achieves substantially higher vaporization rates than in prior art devices without material degradation. Further still, no heater temperature change is required as the source material is consumed.

It is a further advantage of the present invention that it can provide a vapor source in any orientation, which is not possible with prior art devices.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of one embodiment of a device according to the present invention including a piston and a drive mechanism as a way for metering organic material into a heating region;

FIG. 2 shows a graphical representation of vapor pressure vs. temperature for two organic materials;

FIG. 3 is a cross-sectional view of another embodiment of a device according to the present invention including a liquid metal as a way for metering organic material into a heating region and to form a seal to prevent vapors from escaping;

FIG. 4 is a cross-sectional view of a third embodiment of a device according to the present invention including a rotating drum having a surface pattern of recesses as a way for metering organic material into a heating region;

FIG. 5 is a cross-sectional view of a device according to the present invention including a deposition chamber enclosing a substrate; and

FIG. 6 is a cross-sectional view of an OLED device structure that can be prepared with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Turning now to FIG. 1, there is shown a cross-sectional view of
5   one embodiment of a device of this disclosure. Vaporization apparatus **5** is a device for vaporizing organic materials onto a substrate surface to form a film, and includes a first heating region **25** and a second heating region **35** spaced from first heating region **25**. First heating region **25** includes a first heating means represented by base block **20**, which can be a heating base block or a cooling base
10   block, or both, and which can include control passage **30**. Chamber **15** can receive a quantity of organic material **10**. Second heating region **35** includes the region bounded by manifold **60** and permeable member **40**, which can be part of manifold **60**. Manifold **60** also includes one or more apertures **90**. A way of metering organic material includes chamber **15** for receiving the organic material
15   **10**, piston **50** for raising organic material **10** in chamber **15**, as well as permeable member **40**. Vaporization apparatus **5** also includes one or more shields **70**.

Organic material **10** is preferably either a compacted or pre-condensed solid. However, organic material in powder form is also acceptable. Organic material **10** can comprise a single component, or can comprise two or
20   more organic components, each one having a different vaporization temperature. Organic material **10** is in close thermal contact with the first heating means that is base block **20**. Control passages **30** through this block permit the flow of a temperature control fluid, that is, a fluid adapted to either absorb heat from or deliver heat to the first heating region **25**. The fluid can be a gas or a liquid or a
25   mixed phase. Vaporization apparatus **5** includes a way for pumping fluid through control passages **30**. Such pumping means, not shown, are well known to those skilled in the art. Through such means, organic material **10** is heated in first heating region **25** until it is a temperature below its vaporization temperature. The vaporization temperature can be determined by various ways. For example, FIG. 2
30   shows a graphical representation of vapor pressure versus temperature for two organic materials commonly used in OLED devices. The vaporization rate is

proportional to the vapor pressure, so for a desired vaporization rate, the data in FIG. 2 can be used to define the required heating temperature corresponding to the desired vaporization rate. First heating region 25 is maintained at a constant heater temperature as organic material 10 is consumed.

5   Organic material 10 is metered at a controlled rate from first heating region 25 to second heating region 35. Second heating region 35 is heated to a temperature above the vaporization temperature of organic material 10, or each of the organic components thereof. Because a given organic component vaporizes at different rates over a continuum of temperatures, there is a

10   logarithmic dependence of vaporization rate on temperature. In choosing a desired deposition rate, one also determines a necessary vaporization temperature of organic material 10, which will be referred to as the desired rate-dependent vaporization temperature. The temperature of first heating region 25 is below the vaporization temperature, while the temperature of second heating region 35 is at

15   or above the desired rate-dependent vaporization temperature. In this embodiment, second heating region 35 comprises the region bounded by manifold 60 and permeable member 40. Organic material 10 is pushed against permeable member 40 by piston 50, which can be controlled through a force-controlled drive mechanism. Piston 50, chamber 15, and the force-controlled drive mechanism

20   comprise a way for metering. This metering means permits organic material 10 to be metered through permeable member 40 into second heating region 35 at a controlled rate that varies linearly with the vaporization rate. Along with the temperature of second heating region 35, this permits finer rate control of the vaporization rate of organic material 10 and additionally offers an independent

25   measure of the vaporization rate. A thin cross-section of organic material 10 is heated to the desired rate-dependent temperature, which is the temperature of second heating region 35, by virtue of contact and thermal conduction, whereby the thin cross-section of organic material 10 vaporizes. In the case where organic material 10 comprises two or more organic components, the temperature of second

30   heating region 35 is chosen to be above the vaporization temperature of each of the components so that each of the organic material 10 components

simultaneously vaporizes. A steep thermal gradient on the order of 200°C/mm is produced through the thickness of organic material **10**. This gradient protects all but the immediately vaporizing material from the high temperatures. The vaporized organic vapors rapidly pass through the permeable member **40** and can

5   enter into a volume of heated gas manifold **60** or pass directly on to the target substrate. Their residence time at the desired vaporization temperature is very short and, as a result, thermal degradation is greatly reduced. The residence time of organic material **10** at elevated temperature, that is, at the rate-dependent vaporization temperature, is orders of magnitude less than prior art devices and

10   methods (seconds vs. hours or days in the prior art), which permits heating organic material **10** to higher temperatures than in the prior art. Thus, the current device and method can achieve substantially higher vaporization rates, without causing appreciable degradation of organic material **10**. The constant vaporization rate, and constant volume of vaporizing organic material **10** maintained in second

15   heating region **35** establish and maintain a constant plume shape. The plume is herein defined as the vapor cloud exiting vaporization device **5**.

Since second heating region **35** is maintained at a higher temperature than first heating region **25**, it is possible that heat from second heating region **35** can raise the temperature of the bulk of organic material **10**

20   above that of first heating region **25**. Therefore, it is necessary that the first heating means can also cool organic material **10** after it rises above a predetermined temperature. This can be accomplished by varying the temperature of the fluid in control passage **30**.

Where a manifold **60** is used, a pressure develops as vaporization

25   continues and streams of vapor exit the manifold **60** through the series of apertures **90**. The conductance along the length of the manifold is designed to be roughly two orders of magnitude larger than the sum of the aperture conductances as described in commonly assigned U.S. Patent Application Serial No. 10/352,558 filed January 28, 2003 by Jeremy M. Grace et al., entitled "Method of Designing a

30   Thermal Physical Vapor Deposition System", the disclosure of which is herein incorporated by reference. This conductance ratio promotes good pressure

uniformity within manifold **60** and thereby minimizes flow non-uniformities through apertures **90** distributed along the length of the source despite potential local non-uniformities in vaporization rate.

One or more heat shields **70** are located adjacent the heated manifold **60** for the purpose of reducing the heat radiated to the facing target substrate. These heat shields are thermally connected to base block **20** for the purpose of drawing heat away from the shields. The upper portion of shields **70** is designed to lie below the plane of the apertures for the purpose of minimizing vapor condensation on their relatively cool surfaces.

Because only a small portion of organic material **10**, the portion resident in second heating region **35**, is heated to the rate-dependent vaporization temperature, while the bulk of the material is kept well below the vaporization temperature, it is possible to interrupt the vaporization by a way of interrupting heating in second heating region **35**, e.g. stopping the movement of piston **50**. This can be done when a substrate surface is not being coated so as to conserve organic material **10** and minimize contamination of any associated apparatus, such as the walls of a deposition chamber, which will be described below.

Because permeable member **40** can be a fine mesh screen that prevents powder or compacted material from passing freely through it, vaporization apparatus **5** can be used in any orientation. For example, vaporization apparatus **5** can be oriented 180° from what is shown in FIG. 1 so as to coat a substrate placed below it. This is an advantage not found in the heating boats of the prior art.

Although one preferred embodiment has been the use of vaporization apparatus **5** with a powder or compressed material that sublimes when heated, in some embodiments organic material **10** can be a material that liquefies before vaporization, and can be a liquid at the temperature of first heating region **25**. In such a case, permeable member **40** can absorb and retain liquefied organic material **10** in a controllable manner via capillary action, thus permitting control of vaporization rate.

In practice, vaporization apparatus 5 can be used as follows. A quantity of organic material 10, which can comprise one or more components, is provided into chamber 15 of vaporization apparatus 5. In first heating region 25, organic material 10 is actively maintained below the vaporization temperature of each of its organic components. Second heating region 35 is heated to a temperature above the vaporization temperature of organic material 10 or each of the components thereof. Organic material 10 is metered at a controlled rate from first heating region 25 to second heating region 35. A thin cross-section of organic material 10 is heated at a desired rate-dependent vaporization temperature, whereby organic material 10 vaporizes and forms a film on a substrate surface. When organic material 10 comprises multiple components, each component simultaneously vaporizes.

FIG. 3 shows a cross-sectional view of a second embodiment of a device of this disclosure. Vaporization apparatus 45 includes first heating region 25, second heating region 35, base block 20, control passages 30, chamber 15, manifold 60, apertures 90, shields 70, and permeable member 40 as described above. Vaporization apparatus 45 does not include a piston, but instead includes liquid 65.

Organic material 10 can be as described above and is in close thermal contact with base block 20. Organic material 10 is metered at a controlled rate from first heating region 25 to second heating region 35, which is heated to a temperature above the vaporization temperature of organic material 10, or each of the components thereof. Organic material 10 is pushed against permeable member 40 through contact with a low vapor pressure liquid 65. Liquid 65 must be a liquid at the operating temperature of vaporization apparatus 45. For example, many organic materials commonly used in OLED devices have a vaporization temperature over 150°C. Therefore, it is sufficient that liquid 65 can be liquid at 150°C for such organic materials. Liquid 65 can provide very good thermal contact and a vapor-tight seal between organic material 10 and base block 20. Low-melting liquid metals are suitable for this purpose, including gallium, alloys of gallium and indium, as well as controlled expansion alloys of bismuth and indium.

These materials have high thermal conductivity and serve to provide very good thermal contact and a vapor-tight seal between the organic material and the cooling block. Also suitable are low-vapor-pressure oils. Other materials are acceptable as liquid **65** to the extent that they do not react with the organic

5 material **10**, have a higher density than organic material **10**, and have a vapor pressure much lower than the vapor pressure of organic material **10** over the temperature range employed in vaporization apparatus **5**. Organic material **10** floats on the surfaces of such high surface tension, dense liquids and can be pushed against permeable member **40** with a very controllable force. This

10 controlled force, along with the temperature of permeable member **40**, permits precise control of the vaporization rate of the organic material. A thin cross-section of organic material **10** is heated to a desired rate-dependent temperature, that is, the temperature of permeable member **40**, by virtue of contact and thermal conduction, whereby the thin cross-section of organic material **10** vaporizes. A

15 steep thermal gradient on the order of 200°C/mm is produced through the thickness of organic material **10**. This gradient protects all but the immediately vaporizing material from the high temperatures. The vaporized organic vapors rapidly pass through the permeable member **40** and can enter into a volume of heated gas manifold **60** or pass directly on to the target substrate. Their residence

20 time at the desired vaporization temperature is very short and, as a result, thermal degradation is greatly reduced.

Where a manifold **60** is used, a pressure develops as vaporization continues and streams of vapor exit the manifold **60** through the series of apertures **90**. The conductance along the length of the manifold is designed to be roughly

25 two orders of magnitude larger than the sum of the aperture conductances as described by Grace et al. This conductance ratio promotes good pressure uniformity within manifold **60** and thereby minimizes flow non-uniformities through apertures **90** distributed along the length of the source, despite potential local non-uniformities in vaporization rate.

30 Like vaporization apparatus **5**, vaporization apparatus **45** can be adapted to the use of a liquid organic material **10**.

FIG. 4 shows a cross-sectional view of a third embodiment of a device of this disclosure. Vaporization apparatus 55 includes first heating region 25, base block 20, control passages 30, chamber 15, manifold 60, and apertures 90 as described above.

5   Organic material 10 can be as described above and is in close thermal contact with base block 20. Organic material 10 is pushed by either a piston or a liquid as described above against the periphery of rotating drum 105 and is carried as a fine powder film from first heating region 25 to second heating region 35. The powder can be attracted to the drum by electrostatic forces and

10   rotating drum 105 can have surface features such as a knurled pattern or a pattern of small recesses having a definite volume in which a controlled volume of organic material 10 is contained so as to transport a fixed volume of powder. A wiper can optionally be used to remove excess powder from the surface of rotating drum 105. Rotating drum 105 is preferably constructed such that its surface has

15   very little thermal mass, that is, the surface of rotating drum 105 is rapidly heated as it rotates to second heating region 35 and rapidly cools as it rotates back to first heating region 25.

          Second heating region 35 includes a second heating means. The second heating means can be incorporated in the surface of rotating drum 105

20   through induction or RF coupling, it can include a radiant heating element in close proximity to the surface of rotating drum 105, or it can include resistance heating means. The vaporization rate in this embodiment is controlled by the rate of rotation of rotating drum 105, and the quantity of organic material 10 carried on its surface. The heating mechanism simply insures that substantially all of organic

25   material 10 on the surface of rotating drum 105 is transformed to the vapor state. The vaporized organic vapors rapidly pass through second heating region 35, and can enter into a volume of heated gas manifold 60 or pass directly on to the target substrate. Their residence time at temperature is very short and, as a result, thermal degradation is greatly reduced.

30   Where a manifold 60 is used, a pressure develops as vaporization continues and streams of vapor exit the manifold 60 through the series of apertures

90. The conductance along the length of the manifold is designed to be roughly two orders of magnitude larger than the sum of the aperture conductances as described in commonly assigned U.S. Patent Application Serial No. 10/352,558 filed January 28, 2003 by Jeremy M. Grace et al., entitled "Method of Designing a Thermal Physical Vapor Deposition System", the disclosure of which is herein incorporated by reference. This conductance ratio promotes good pressure uniformity within manifold **60** and thereby minimizes flow non-uniformities through apertures **90** distributed along the length of the source, despite potential local non-uniformities in vaporization rate.

Like vaporization apparatus **5**, vaporization apparatus **45** can be adapted to the use of a liquid organic material **10**.

Turning now to FIG. 5, there is shown an embodiment of a device of this disclosure including a deposition chamber enclosing a substrate. Deposition chamber **80** is an enclosed apparatus that permits an OLED substrate **85** to be coated with organic material **10** transferred from vaporization apparatus **5**. Deposition chamber **80** is held under controlled conditions, e.g. a pressure of 1 Torr or less provided by vacuum source **100**. Deposition chamber **80** includes load lock **75** which can be used to load uncoated OLED substrates **85**, and unload coated OLED substrates. OLED substrate **85** can be moved by translational apparatus **95** to provide even coating of vaporized organic material **10** over the entire surface of OLED substrate **85**. Although vaporization apparatus is shown as partially enclosed by deposition chamber **80**, it will be understood that other arrangements are possible, including arrangements wherein vaporization apparatus **5** is entirely enclosed by deposition chamber **80**.

In practice, an OLED substrate **85** is placed in deposition chamber **80** via load lock **75** and held by translational apparatus **95** or associated apparatus. Vaporization apparatus **5** is operated as described above, and translational apparatus **95** moves OLED substrate **85** perpendicular to the direction of emission of organic material **10** vapors from vaporization apparatus **5**, thus forming a film of organic material **10** on the surface of OLED substrate **85**.

Turning now to FIG. 6, there is shown a cross-sectional view of a pixel of a light-emitting OLED device **110** that can be prepared in part according to the present invention. The OLED device **110** includes at a minimum a substrate **120**, a cathode **190**, an anode **130** spaced from cathode **190**, and a light-emitting

5 layer **150**. The OLED device can also include a hole-injecting layer **135**, a hole-transporting layer **140**, an electron-transporting layer **155**, and an electron-injecting layer **160**. Hole-injecting layer **135**, hole-transporting layer **140**, light-emitting layer **150**, electron-transporting layer **155**, and electron-injecting layer **160** comprise a series of organic layers **170** disposed between anode **130** and

10 cathode **190**. Organic layers **170** are the layers most desirably deposited by the device and method of this invention. These components will be described in more detail.

Substrate **120** can be an organic solid, an inorganic solid, or include organic and inorganic solids. Substrate **120** can be rigid or flexible and can be

15 processed as separate individual pieces, such as sheets or wafers, or as a continuous roll. Typical substrate materials include glass, plastic, metal, ceramic, semiconductor, metal oxide, semiconductor oxide, semiconductor nitride, or combinations thereof. Substrate **120** can be a homogeneous mixture of materials, a composite of materials, or multiple layers of materials. Substrate **120** can be an

20 OLED substrate, that is a substrate commonly used for preparing OLED devices, e.g. active-matrix low-temperature polysilicon or amorphous-silicon TFT substrate. The substrate **120** can either be light transmissive or opaque, depending on the intended direction of light emission. The light transmissive property is desirable for viewing the EL emission through the substrate. Transparent glass or

25 plastic are commonly employed in such cases. For applications where the EL emission is viewed through the top electrode, the transmissive characteristic of the bottom support is immaterial, and therefore can be light transmissive, light absorbing or light reflective. Substrates for use in this case include, but are not limited to, glass, plastic, semiconductor materials, ceramics, and circuit board

30 materials, or any others commonly used in the formation of OLED devices, which can be either passive-matrix devices or active-matrix devices.

An electrode is formed over substrate **120** and is most commonly configured as an anode **130**. When EL emission is viewed through the substrate **120**, anode **130** should be transparent or substantially transparent to the emission of interest. Common transparent anode materials useful in this invention are

5   indium-tin oxide and tin oxide, but other metal oxides can work including, but not limited to, aluminum- or indium-doped zinc oxide, magnesium-indium oxide, and nickel-tungsten oxide. In addition to these oxides, metal nitrides such as gallium nitride, metal selenides such as zinc selenide, and metal sulfides such as zinc sulfide, can be used as an anode material. For applications where EL emission is

10   viewed through the top electrode, the transmissive characteristics of the anode material are immaterial and any conductive material can be used, transparent, opaque or reflective. Example conductors for this application include, but are not limited to, gold, iridium, molybdenum, palladium, and platinum. The preferred anode materials, transmissive or otherwise, have a work function of 4.1 eV or

15   greater. Desired anode materials can be deposited by any suitable way such as evaporation, sputtering, chemical vapor deposition, or electrochemical means. Anode materials can be patterned using well known photolithographic processes.

While not always necessary, it is often useful that a hole-injecting layer **135** be formed over anode **130** in an organic light-emitting display. The hole-

20   injecting material can serve to improve the film formation property of subsequent organic layers and to facilitate injection of holes into the hole-transporting layer. Suitable materials for use in hole-injecting layer **135** include, but are not limited to, porphyrinic compounds as described in U.S. Patent 4,720,432, plasma-deposited fluorocarbon polymers as described in U.S. Patent 6,208,075, and

25   inorganic oxides including vanadium oxide (VOx), molybdenum oxide (MoOx), nickel oxide (NiOx), etc. Alternative hole-injecting materials reportedly useful in organic EL devices are described in EP 0 891 121 A1 and EP 1 029 909 A1.

While not always necessary, it is often useful that a hole-transporting layer **140** be formed and disposed over anode **130**. Desired hole-

30   transporting materials can be deposited by any suitable way such as evaporation, sputtering, chemical vapor deposition, electrochemical means, thermal transfer, or

laser thermal transfer from a donor material, and can be deposited by the device and method described herein. Hole-transporting materials useful in hole-transporting layer **140** are well known to include compounds such as an aromatic tertiary amine, where the latter is understood to be a compound containing at least one trivalent nitrogen atom that is bonded only to carbon atoms, at least one of which is a member of an aromatic ring. In one form the aromatic tertiary amine can be an arylamine, such as a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylamines are illustrated by Klupfel et al. in U.S. Patent 3,180,730. Other suitable triarylamines substituted with one or more vinyl radicals and/or comprising at least one active hydrogen-containing group are disclosed by Brantley et al. in U.S. Patents 3,567,450 and 3,658,520.

A more preferred class of aromatic tertiary amines are those which include at least two aromatic tertiary amine moieties as described in U.S. Patents 4,720,432 and 5,061,569. Such compounds include those represented by structural Formula A

$$A \qquad Q_1\diagdown_G\diagup Q_2$$

wherein:

Q_1 and Q_2 are independently selected aromatic tertiary amine moieties; and

G is a linking group such as an arylene, cycloalkylene, or alkylene group of a carbon to carbon bond.

In one embodiment, at least one of Q1 or Q2 contains a polycyclic fused ring structure, e.g., a naphthalene. When G is an aryl group, it is conveniently a phenylene, biphenylene, or naphthalene moiety.

A useful class of triarylamines satisfying structural Formula A and containing two triarylamine moieties is represented by structural Formula B

$$B \qquad R_1 - \underset{\underset{R_4}{\overset{\overset{R_2}{|}}{\underset{}{|}}}{C} - R_3$$
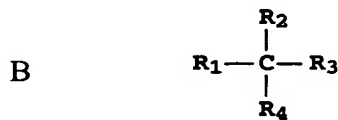
where:

R$_1$ and R$_2$ each independently represent a hydrogen atom, an aryl group, or an alkyl group or R$_1$ and R$_2$ together represent the atoms completing a cycloalkyl group; and

5   R$_3$ and R$_4$ each independently represent an aryl group, which is in turn substituted with a diaryl substituted amino group, as indicated by structural Formula C

C

$$R_5 \diagdown \atop R_6 \diagup N \text{---}$$

wherein R$_5$ and R$_6$ are independently selected aryl groups. In one embodiment, at least one of R$_5$ or R$_6$ contains a polycyclic fused ring structure, e.g., a naphthalene.

10   Another class of aromatic tertiary amines are the tetraaryldiamines. Desirable tetraaryldiamines include two diarylamino groups, such as indicated by Formula C, linked through an arylene group. Useful tetraaryldiamines include those represented by Formula D

D

$$R_7 \diagdown \atop Ar \diagup N \text{---} \left(\text{---} Are \text{---} \right)_n \text{---} N \diagup R_8 \atop \diagdown R_9$$
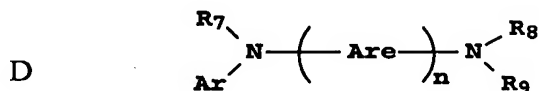
wherein:

15   each Are is an independently selected arylene group, such as a phenylene or anthracene moiety;

n is an integer of from 1 to 4; and

Ar, R$_7$, R$_8$, and R$_9$ are independently selected aryl groups.

In a typical embodiment, at least one of Ar, R$_7$, R$_8$, and R$_9$ is a

20   polycyclic fused ring structure, e.g., a naphthalene.

The various alkyl, alkylene, aryl, and arylene moieties of the foregoing structural Formulae A, B, C, D, can each in turn be substituted. Typical substituents include alkyl groups, alkoxy groups, aryl groups, aryloxy groups, and halogens such as fluoride, chloride, and bromide. The various alkyl and alkylene

25   moieties typically contain from 1 to about 6 carbon atoms. The cycloalkyl moieties can contain from 3 to about 10 carbon atoms, but typically contain five, six, or

seven carbon atoms--e.g., cyclopentyl, cyclohexyl, and cycloheptyl ring structures. The aryl and arylene moieties are usually phenyl and phenylene moieties.

The hole-transporting layer in an OLED device can be formed of a single or a mixture of aromatic tertiary amine compounds. Specifically, one can

5   employ a triarylamine, such as a triarylamine satisfying the Formula B, in combination with a tetraaryldiamine, such as indicated by Formula D. When a triarylamine is employed in combination with a tetraaryldiamine, the latter is positioned as a layer interposed between the triarylamine and the electron-injecting and transporting layer. The device and method described herein can be

10   used to deposit single- or multi-component layers, and can be used to sequentially deposit multiple layers.

Another class of useful hole-transporting materials includes polycyclic aromatic compounds as described in EP 1 009 041. In addition, polymeric hole-transporting materials can be used such as poly(N-vinylcarbazole)

15   (PVK), polythiophenes, polypyrrole, polyaniline, and copolymers such as poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) also called PEDOT/PSS.

Light-emitting layer 150 produces light in response to hole-electron recombination. Light-emitting layer 150 is commonly disposed over hole-

20   transporting layer 140. Desired organic light-emitting materials can be deposited by any suitable way such as evaporation, sputtering, chemical vapor deposition, electrochemical means, or radiation thermal transfer from a donor material, and can be deposited by the device and method described herein. Useful organic light-emitting materials are well known. As more fully described in U.S. Patents

25   4,769,292 and 5,935,721, the light-emitting layers of the organic EL element comprise a luminescent or fluorescent material where electroluminescence is produced as a result of electron-hole pair recombination in this region. The light-emitting layers can be comprised of a single material, but more commonly include a host material doped with a guest compound or dopant where light emission

30   comes primarily from the dopant. The dopant is selected to produce color light having a particular spectrum. The host materials in the light-emitting layers can be

an electron-transporting material, as defined below, a hole-transporting material, as defined above, or another material that supports hole-electron recombination. The dopant is usually chosen from highly fluorescent dyes, but phosphorescent compounds, e.g., transition metal complexes as described in WO 98/55561,

5   WO 00/18851, WO 00/57676, and WO 00/70655 are also useful. Dopants are typically coated as 0.01 to 10 % by weight into the host material. The device and method described herein can be used to coat multi-component guest/host layers without the need for multiple vaporization sources.

Host and emitting molecules known to be of use include, but are

10   not limited to, those disclosed in U.S. Patents 4,768,292; 5,141,671; 5,150,006; 5,151,629; 5,294,870; 5,405,709; 5,484,922; 5,593,788; 5,645,948; 5,683,823; 5,755,999; 5,928,802; 5,935,720; 5,935,721; and 6,020,078.

Metal complexes of 8-hydroxyquinoline and similar derivatives (Formula E) constitute one class of useful host materials capable of supporting

15   electroluminescence, and are particularly suitable for light emission of wavelengths longer than 500 nm, e.g., green, yellow, orange, and red.

E
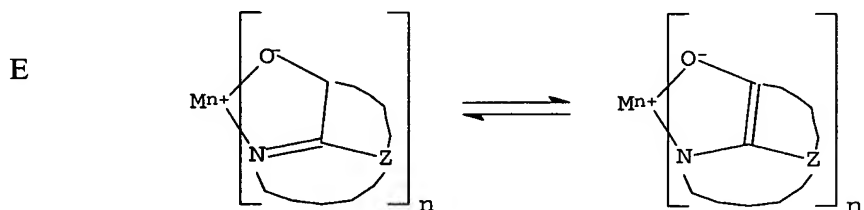
wherein:

M represents a metal;

n is an integer of from 1 to 3; and

20   Z independently in each occurrence represents the atoms completing a nucleus having at least two fused aromatic rings.

From the foregoing it is apparent that the metal can be a monovalent, divalent, or trivalent metal. The metal can, for example, be an alkali metal, such as lithium, sodium, or potassium; an alkaline earth metal, such as

25   magnesium or calcium; or an earth metal, such as boron or aluminum. Generally

any monovalent, divalent, or trivalent metal known to be a useful chelating metal can be employed.

Z completes a heterocyclic nucleus containing at least two fused aromatic rings, at least one of which is an azole or azine ring. Additional rings, including both aliphatic and aromatic rings, can be fused with the two required rings, if required. To avoid adding molecular bulk without improving on function the number of ring atoms is usually maintained at 18 or less.

The host material in light-emitting layer **150** can be an anthracene derivative having hydrocarbon or substituted hydrocarbon substituents at the 9 and 10 positions. For example, derivatives of 9,10-di-(2-naphthyl)anthracene constitute one class of useful host materials capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 400 nm, e.g., blue, green, yellow, orange or red.

Benzazole derivatives constitute another class of useful host materials capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 400 nm, e.g., blue, green, yellow, orange or red. An example of a useful benzazole is 2, 2', 2"-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole].

Desirable fluorescent dopants include perylene or derivatives of perylene, derivatives of anthracene, tetracene, xanthene, rubrene, coumarin, rhodamine, quinacridone, dicyanomethylenepyran compounds, thiopyran compounds, polymethine compounds, pyrilium and thiapyrilium compounds, derivatives of distryrylbenzene or distyrylbiphenyl, bis(azinyl)methane boron complex compounds, and carbostyryl compounds.

Other organic emissive materials can be polymeric substances, e.g. polyphenylenevinylene derivatives, dialkoxy-polyphenylenevinylenes, poly-para-phenylene derivatives, and polyfluorene derivatives, as taught by Wolk et al. in commonly assigned U.S. Patent 6,194,119 B1 and references cited therein.

While not always necessary, it is often useful that OLED device **110** includes an electron-transporting layer **155** disposed over light-emitting layer **150**. Desired electron-transporting materials can be deposited by any suitable way

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such as evaporation, sputtering, chemical vapor deposition, electrochemical means, thermal transfer, or laser thermal transfer from a donor material, and can be deposited by the device and method described herein. Preferred electron-transporting materials for use in electron-transporting layer **155** are metal chelated

5   oxinoid compounds, including chelates of oxine itself (also commonly referred to as 8-quinolinol or 8-hydroxyquinoline). Such compounds help to inject and transport electrons and exhibit both high levels of performance and are readily fabricated in the form of thin films. Exemplary of contemplated oxinoid compounds are those satisfying structural Formula E, previously described.

10   Other electron-transporting materials include various butadiene derivatives as disclosed in U.S. Patent 4,356,429 and various heterocyclic optical brighteners as described in U.S. Patent 4,539,507. Benzazoles satisfying structural Formula G are also useful electron-transporting materials.

        Other electron-transporting materials can be polymeric substances,

15   e.g. polyphenylenevinylene derivatives, poly-para-phenylene derivatives, polyfluorene derivatives, polythiophenes, polyacetylenes, and other conductive polymeric organic materials such as those listed in *Handbook of Conductive Molecules and Polymers*, Vols. 1-4, H.S. Nalwa, ed., John Wiley and Sons, Chichester (1997).

20   An electron-injecting layer **160** can also be present between the cathode and the electron-transporting layer. Examples of electron-injecting materials include alkaline or alkaline earth metals, alkali halide salts, such as LiF mentioned above, or alkaline or alkaline earth metal doped organic layers.

        Cathode **190** is formed over the electron-transporting layer **155** or

25   over light-emitting layer **150** if an electron-transporting layer is not used. When light emission is through the anode **130**, the cathode material can be comprised of nearly any conductive material. Desirable materials have good film-forming properties to ensure good contact with the underlying organic layer, promote electron injection at low voltage, and have good stability. Useful cathode materials

30   often contain a low work function metal (< 3.0 eV) or metal alloy. One preferred cathode material is comprised of a Mg:Ag alloy wherein the percentage of silver is

in the range of 1 to 20 %, as described in U.S. Patent 4,885,221. Another suitable class of cathode materials includes bilayers comprised of a thin layer of a low work function metal or metal salt capped with a thicker layer of conductive metal. One such cathode is comprised of a thin layer of LiF followed by a thicker layer of Al as described in U.S. Patent 5,677,572. Other useful cathode materials include, but are not limited to, those disclosed in U.S. Patents 5,059,861; 5,059,862; and 6,140,763.

When light emission is viewed through cathode **190**, it must be transparent or nearly transparent. For such applications, metals must be thin or one must use transparent conductive oxides, or include these materials. Optically transparent cathodes have been described in more detail in U.S. Patent 5,776,623. Cathode materials can be deposited by evaporation, sputtering, or chemical vapor deposition. When needed, patterning can be achieved through many well known methods including, but not limited to, through-mask deposition, integral shadow masking as described in U.S. Patent 5,276,380 and EP 0 732 868, laser ablation, and selective chemical vapor deposition.

Cathode materials can be deposited by evaporation, sputtering, or chemical vapor deposition. When needed, patterning can be achieved through many well known methods including, but not limited to, through-mask deposition, integral shadow masking as described in U.S. Patent 5,276,380 and EP 0 732 868, laser ablation, and selective chemical vapor deposition.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

PARTS LIST

5	vaporization apparatus
10	organic material
15	chamber
20	base block
25	first heating region
30	control passage
35	second heating region
40	permeable member
45	vaporization apparatus
50	piston
55	vaporization apparatus
60	manifold
65	liquid
70	shield
75	load lock
80	deposition chamber
85	OLED substrate
90	aperture
95	translational apparatus
100	vacuum source
105	rotating drum
110	OLED device
120	substrate
130	anode
135	hole-injecting layer
140	hole-transporting layer
150	light-emitting layer
155	electron-transporting layer

160	electron-injecting layer
170	organic layers
190	cathode